Uranium(VI) Sorption and Diffusion in Montmorillonite and Bentonite: Experiments and Modeling

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The long-term management of nuclear waste requires reliable predictions of radionuclide transport through engineered barrier systems (EBS).

- **Compacted bentonite** (montmorillonite) is the proposed backfill material in EBS.

- **Diffusion** will be the dominant transport mechanism in EBS that contributes to radionuclide dose in the environment.

- **Gradients of chemical solution conditions and temperature** are expected over time and across EBS.

**Goals:**

- Decrease the uncertainty in actinide sorption/diffusion sub-models that are part of performance assessment models for waste repositories.

- Investigate effects of changing chemical conditions and temperatures on uranium(VI) sorption and diffusion.
**Montmorillonite**

- **Two sorption sites/surface reactions:**
  - Cation exchange on basal surfaces
  - Surface complexation on edge sites

- **Two porosities/diffusion pathways:**
  - Macropores between clay particles
  - Small (1-3 nm) interlayer spaces within clay particles

**Uranium(VI)**

- Uranium(VI) can be present as *cationic*, *anionic* or *neutral species* in solution.

System conditions affect sorption mechanisms and diffusion accessible porosities.
**Experimental setup:**
- Through-diffusion experiment
- Na-montmorillonite at 0.8 g/cm³
- Solute: 2.35 μM U(VI)\textsubscript{Tot}
- Target pH 8.75 or pH 8.95
- I=0.1 M NaCl/NaHCO\textsubscript{3}
- Flow-rate: ~0.7 ml/min

**Solution analysis to characterize:**
- U(VI) flux: U-233 (LSC)
- U(VI) speciation:
  - pH,
  - Ca, Fe, Si, Al, etc. (ICP-MS),
  - Total alkalinity (titrations)

**Experimental steps:**
- pH-equilibration of clay (batch): 3 weeks
- Saturation of dry, packed clay: ~3 ½ weeks
- Through-diffusion of HTO tracer: ~2 weeks
- Through-diffusion of U(VI): 11 weeks
Uranium(VI) Diffusion Experiments: Results

- Decrease in U(VI) flux relative to HTO flux.
- Indication for exclusion of anionic U(VI) species from clay interlayer spaces.

**Experimentally-determined normalized flux (m d⁻¹):**

\[
J_i = \frac{C_{\text{low}}}{C_{\text{high}}} \frac{V_{\text{low}}}{A\Delta t}
\]

**Fick’s 1st law:**

\[
J_i = -\varepsilon_{a,i} \frac{D_{w,i}}{G_i} \frac{dc_i}{dx}
\]

\[\varepsilon_{a,i} \ldots \text{diffusion-accessible porosity} \]

\[G_i \ldots \text{constructivity/(tortuosity)}^2\]
Uranium(VI) Diffusion Experiments: Results

Estimated $U$(VI) $K_d$ values:
- pH-8.75: 2.0 [L/kg]
- pH-8.95: 1.3 [L/kg]

- Uranium(VI) retardation under both pH conditions: $K_d, \text{pH-8.75} > K_d, \text{pH-8.95}$.
- U(VI) sorption due to (strong) surface complexation, not (weak) cation exchange.
- Apparent kinetic limitations for U(VI) sorption at pH-8.75 relative to pH-8.95.
Summary: U(VI)-Montmorillonite Sorption Experiments

**Experimental setup:**
- 0.5 g/L Na-montmorillonite
- \( I = 0.1 \text{ M NaCl/NaHCO}_3 \)
- Sorption over: 48.5 hours
- Analysis of supernatant sol.:
  - pH
  - U-238
  - Total Inorganic Carbon (TIC)
  - Other metals: Ca, Mg, Si, Al, etc.

**Experimental conditions:**
Peculiarities of Montmorillonite Relevant for Development of Surface Complexation Models

- Surface complexation models (SCMs) originally developed for simple mineral oxides.
- Metal surface complexation reaction:
  \[ > \text{SOH} + \text{Me}^+ \leftrightarrow \text{SOMe} + \text{H}^+ \]
  \[ \Delta G_{\text{tot}} = \Delta G_{\text{chem}}^0 + \Delta G_{\text{coul}}^0 \]

\[ K = \frac{[> \text{SOMe}][H^+]}{[> \text{SOH}]} \exp \left( \frac{-F\psi}{RT} \right) \]

- Needed: Knowledge of surface potential as a function of pH, ionic strength, electrolyte
- For mineral oxides:
  Determine parameters based on potentiometric titrations of solid
- Montmorillonite: Spillover effect

\[ (\equiv \text{Al}_{\text{Oc}-\text{OH}_2})(\equiv \text{Si}_1\text{Al}_{\text{Oc}}\text{O}) \]
**Surface model:**
- Mean-field approach to describe relationship between surface charge and surface potential (Bourg, et al., 2007; Tournassat et al., 2013):
  \[
  \frac{F \psi_{edge}}{RT} = A_1 a \sinh(A_2 (Q_{edge} + A_3))
  \]
  - \(A_1, A_2, A_3\) … fitted parameters, \(f(I)\)
  - \(Q_{edge}\) … surface charge of edge site
- Protonation/deprotonation constants from first-principle molecular dynamics (Liu et al., 2015)

**Uranium(VI) sorption:**
- Modification of PHREEQC to include clay surface potential model.
- No ion exchange reactions considered due to high ionic strength in sorption experiments.
- Modeling steps:
  1. Fitting of surface complexation constants using U(VI) sorption data from ‘CO2-free’ exp.
  2. Blind fit of U(VI) sorption under atmospheric \(P_{CO2}\): This study and literature data
  3. Evaluation of relevance of ternary U(VI)-carbonato surface complexes
Results: Surface Complexation Modeling

Step 1: Fitting of surface complexation constants using U(VI) sorption data from ‘CO₂-free’ experiment only

\[ \text{SOH}_3 + UO_2^{2+} = \text{SOH}_3 UO_2^{2+} \quad \log K = 3.8 \]

\[ \text{SOH}_3 + UO_2^{2+} = \text{SOHUO}_2 + 2 H^+ \quad \log K = -5 \]

\[ \text{SOH}_3 + UO_2^{2+} + 2 H_2O = \text{SOUO}_2(OH)_2^{-3} + 5 H^+ \quad \log K = -25.4 \]

>SOH₃ edge site:
(≡Siₜ-OH)(≡Alₒc-OH₂)(≡SiₜAlₒc-O)
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1E-6 M U(VI)$_{Tot}$, 2.1 mM Ca
Turner, 1996

Hyun, 2001

Troyer, 2016,
\( \text{pH 6} \)
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\begin{align*}
\text{nate concentrations:} & \\
\text{efficient.}
\end{align*}

by electrostatic SCM.
Summary: This Year’s Accomplishments

Technical:

**U(VI) diffusion:** Completion of diffusion experiment in Na-montmorillonite at alkaline pH.
- Uranium(VI) retardation due to sorption reactions.
- First direct experimental evidence for U(VI) anion exclusion effects.

**U(VI) sorption modeling:**
Development of non-electrostatic and electrostatic SCMs for U(VI) sorption onto Na-montmorillonite.
- Electrostatic SCM including “spillover” effect decreases number of fitting parameters needed (3 versus 10 surface complexes).
- Formation of ternary U(VI)-carbonato surface complexes was not supported by electrostatic SCM.

Publications: *(UFD funded authors in bold)*


Conference Presentations:
- **Colloque du Groupe Français des Argiles**, May 2016, Poitiers, France.
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Outlook: Plans for Future Experiments
Heat Effects and Increase in Solid Complexity

**Motivation:**

Potential changes in U(VI) sorption due to heat effects on bentonite

Microstructure characterization of FEBEX bentonite: Synchrotron X-ray microtomography (M. Voltolini, LBNL)

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**Research Questions / Experimental Plans:**

**U(VI) sorption:**

- Do U(VI) sorption affinities change after heat-treatment?
- Role of mineral ‘impurities’ for overall U(VI) sorption behavior?

**U(VI) diffusion/mobility:**

- Does fracture network alter overall U(VI) transport behavior (flux and breakthrough)?
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<th>Used Fuel Disposition</th>
<th>Additional slides</th>
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Structural complexity of Na-montmorillonite affects clay porosity

2 types of porosities and diffusion pathways due to clay structure:
- Small (1-3 nm) interlayer spaces within clay particles
- Macropores between clay particles

System conditions affect diffusion-accessible porosities.

Negative clay surface charges lead to:
- Cation sorption by ion exchange reactions
- Potential exclusion of anions from interlayer spaces
Implications of System Complexities for Uranium(VI) Diffusion

**Fick’s 1st law:**

\[
J_i = -D_{a,i} \left( \varepsilon_{a,i} + \rho_b K_{d,i} \right) \frac{dc_i}{dx}
\]

- \( J_i \)… apparent diffusion coefficient
- \( \varepsilon_{a,i} \)… diffusion-accessible porosity
- \( \rho_b \)… bulk density
- \( K_{d,i} \)… sorption distribution coefficient
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- $\rho_b$ ... bulk density
- $G_i$ ... constructivity/(tortuosity)$^2$
- $K_{d,i}$ ... sorption distribution coefficient

**Anion exclusion from interlayers**

- Decrease in diffusion-accessible porosity
- Decrease in diffusive flux

**Graphs:**
- Bromide
- Tritiated water

**Normalized flux [m day$^{-1}$]**

**Time [days]**
Implications of System Complexities for Uranium(VI) Diffusion

Fick’s 1st law:

\[ J_i = -D_{a,i} \left( \varepsilon_{a,i} + \rho_b K_{d,i} \right) \frac{dc_i}{dx} \]

- Decrease in diffusion-accessible porosity
- Decrease in diffusive flux

Anion exclusion from interlayers

Sorption reactions

- Retardation (cation exchange/surf. complex.)
- Weak sorption: Increase in flux
- Strong sorption: No change in flux

\[ D_{a,i} \ldots \text{apparent diffusion coefficient} \]
\[ \varepsilon_{a,i} \ldots \text{diffusion-accessible porosity} \]
\[ \rho_b \ldots \text{bulk density} \]
\[ G_i \ldots \text{constructivity/(tortuosity)}^2 \]
\[ K_{d,i} \ldots \text{sorption distribution coefficient} \]
**Goal:** Evaluate effects of anion exclusion and uranium(VI) sorption reactions.

- Target range of log $K_d$ values: 0.7-1 [L/kg] ($K_d=5$-10 [L/kg])
- Two parallel diffusion experiments at target pH values of pH=8.75 and pH=8.95.
Experimental setup:
- Through-diffusion experiment
- Na-montmorillonite at 0.8 g/cm³
- Solute: 2.35 μM U(VI)\textsubscript{Tot}
- pH~8.69 or pH~8.87
- I=0.1 M NaCl/NaHCO\textsubscript{3}
- Flow-rate: ~0.7 ml/min

Solution analysis to characterize:
- U(VI) flux: U-233 (LSC)
- U(VI) speciation:
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Experimental steps:
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Uranium(VI) Diffusion Experiments: Equilibration of pH Conditions

- Sufficiently stable pH conditions during diffusion experiments.
- Average pH drop less than 0.1 pH-units.
Protonation/deprotonation constants from FPMD calculations (from literature)

Predicted titration curves vs. experimental data
Predicted edge surface charge and potential as a function of pH for montmorillonite particles immersed in 0.001, 0.01, and 0.1 mol·L⁻¹ NaCl background electrolyte. Simulations were carried out with $x_{\text{Si-Al-Si}} = 1$. 
Evaluation of ternary U(VI)-carbonato surface complexes

\[ \text{SOH}_3 + \text{UO}_2^{+2} + \text{HCO}_3^- = \text{SOH}_3\text{UO}_2(\text{CO}_3) + \text{H}^+ \]
\[ \text{log K = 5} \]

\[ \text{SOH}_3 + \text{UO}_2^{+2} + 2 \text{HCO}_3^- = \text{SOH}_2\text{UO}_2(\text{CO}_3)_2^{-3} + 3 \text{H}^+ \]
\[ \text{log K = -1.5} \]

Adsorption model with only 3 (5) reactions in absence (presence) of U-CO3 complexes

For comparison the non-electrostatic model of Marques et al., 2012 has 10 surface complexes

Better description of the system with fewer parameters

In the presence of carbonate, model outcomes are very dependent on CO2 partial pressure

It is necessary to measure this parameter to extract sorption constants for U sorption.
**Uranium (VI) Sorption Studies: Goals, Materials and Setup**

**Goals:**
- Investigate potential impacts of heat-induced mineral alterations in bentonite on U(VI) sorption behavior.
- Provide input parameters for U(VI) diffusion models.

**Solids:**
- ‘Cooked’ and ‘uncooked’ bentonite (EBS-12, LANL)
- Na-montmorillonite as reference (Swy-2, pretreated)

**Experimental conditions:**
- 0.5 g/L solid
- I = 0.1 M NaCl/NaHCO₃
- U(VI)$_{Tot}$: 10⁻⁶ mol/L (U-238)
- Atmospheric CO₂
- Time-dependent sampling over 21 days
- ICP-MS analysis for U-238 and Ca, Fe, Si, Al, etc. (ongoing)
Heat treatment leads to:
• Lower uranium(VI) sorption under circum-neutral pH conditions.